



Tribological performance of hybrid organo-silicate coatings



Amalia Skarmoutsou, Costas A. Charitidis*

School of Chemical Engineering, National Technical University of Athens, 9 Heron Polytechniou St., Zographos, 15780 Athens, Greece

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ABSTRACT

Hybrid organo-silicate coatings (hybrid coatings) present many advantages and find use in many applications. However, their tribological performance has not been widely investigated due to the non-uniformity of the synthesized hybrid materials. In this work, nanoscratch tests have been employed for the investigation of wear mechanisms and organic–inorganic coatings adhesion. The tribological performance was investigated under low applied normal forces, in order to estimate the coefficient of friction (μ) values, the coatings resistance and the humidity effect when the synthesized coatings were submerged on a cell culture medium. Also, the performed plastic deformation was correlated with the experimental data and the surface images taken with a scanning probe microscope after the scratch tests. Furthermore, the experimental data were fitted and the relative coefficient of friction and cohesive force of each synthesized coating were calculated, since organic and hybrid materials do not conform with the classic tribology laws and are greatly affected by the adhesion forces observed between tip and sample's surface.

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1. Introduction

Hybrid organo-silicates materials were firstly reported by Schmidt [1] and Wilkes et al. [2], in the mid-1980s. Through sol–gel process, an organic polymer can be chemically bonded to an inorganic network resulting in polymer-like materials. These hybrid materials exhibit variation in physical properties; namely, the hybrid materials can be brittle and hard or rubbery and soft, because of the differences in the ratio of the organic to the inorganic constituents [3]. The synthetic process leads to the formation of the inorganic network in hybrid materials with special features, resulting in modification of surface properties, such as scratch resistance and wettability [4]. Generally, polymers and their composites (hybrid materials) present strength, lightness, versatility, ease of processing and low cost, and they can replace metals in many applications. Hybrid materials have significant applications ranging from microelectronic devices and aeronautic applications, to low friction fibers for bandages and other prosthetic applications [5], because of their improved surface properties and tribological performance, i.e. the reduced friction and wear [6]. However, their tribological properties have not been, yet, extensively investigated, due to their viscoelastic properties, which render process and analysis complicated.

Nanoscratch tests are a useful technique by which tribology, friction and wear failure are recorded, film or coating delamination is quantified and material scratch resistance and coating adhesion onto substrates are evaluated [7]. Nanoscratch has advantages over other techniques, because it can identify and measure the interface in composite or multiphase materials regions [8]. Scratch resistance and adhesion are characterized by the tip penetration rate and the normal force, at which coating debonds from the substrate. Typical parameters that affect its value are the mechanical properties of the system coating–substrate, the coating's thickness, the tip radius, the loading rate and the friction between indenter and coating's surface [7]. In the present study, the scratch behavior of various hybrid coatings deposited onto silanized glass substrates is presented, in order to calculate their coefficient of friction (μ) values and to estimate their wear resistance. Additionally, the plastic deformation and the possible delamination of the hybrid coatings are observed.

2. Experimental procedure

2.1. Materials

All the chemicals used in this work were obtained by Sigma–Aldrich (Germany). The material used for the fabrication of the coatings is an organic–inorganic composite, produced by the addition of methacryloxypropyl trimethoxysilane (MAPTMS, 99%) to zirconium propoxide (ZPO, 70% in propanol). 2-(dimethylamino)ethyl methacrylate (DMAEMA, >99%) was also

* Corresponding author. Tel.: +30 2107724046.

E-mail address: charitidis@chemeng.ntua.gr (C.A. Charitidis).

Table 1
Hardness (H) and reduced modulus (E_r) values of the synthesized coatings, at the 10% of coatings thickness.

Coatings	As prepared		After submersion	
	H (GPa)	E_r (GPa)	H (GPa)	E_r (GPa)
Organic	0.0283 ± 0.0015	0.505 ± 0.013	–	–
Hybrid 1	1.114 ± 0.0227	2.281 ± 0.0672	0.297 ± 0.016	1.268 ± 0.0132
Hybrid 2	0.527 ± 0.029	3.725 ± 0.0619	0.638 ± 0.0025	7.98 ± 0.0666

added which was copolymerized with MAPTMS upon photopolymerization. ZPO and the alkoxy groups of MAPTMS served as the inorganic network forming moieties. 4,4-bis(diethylamino) benzophenone (BIS) was used as the photoinitiator.

2.2. Coatings synthesis

In this study, three different coatings were studied. Their synthesis has been extensively reported in a previous work [9]. A short description of the synthetic route is following.

- Organic coating:** a PDMAEMA solution in toluene was deposited by spin coating on a glass substrate at 1000 rpm for 30 s. The deposition was repeated totally 4 times.
- Hybrid coatings:** two different hybrid coatings were prepared by drop-casting or spin coating of two different solutions, previously reported in [9], on 100 μm thick glass substrates. Hybrid 1 material is comprised only of MAPTMS and ZPO, and hybrid 2 consists of MPAPTMS, ZPO and DMAEMA (Table 1) [9]. The deposited solutions were dried on a hotplate at 50 °C for 10 min before the photopolymerization (Table 1). The heating process led to the condensation of the alkoxy groups and the formation of the inorganic matrix. The fabrication of hybrid blocks was achieved through Direct fs Laser Writing. Through this method the methacrylate moieties were polymerized using a KrF excimer laser, operating at 248 nm, resulting in the formation of irreversible and fully saturated aliphatic C–C covalent bonds that further increase the connectivity of the material [9–11]. Finally, the samples were developed for 30 min in a 50:50 solution of n-propanol:isopropanol, and were further rinsed with isopropanol. In Fig. 1, a schematic representation of the synthetic process is shown.

2.3. Materials characterization

2.3.1. Nanoindentation tests

Nanoindentation tests were firstly performed on the synthesized materials, in order to choose the appropriate normal forces to apply while scratch testing. The indentation tests were conducted with a Hysitron TriboLab® nanomechanical test instrument and the hardness (H) and the reduced modulus (E_r) of the coatings were determined by the nanoindentation load-displacement data [12], through Oliver–Pharr model [13,14]. Details on the performed nanoindentation tests are presented in our previous work [9].

2.3.2. Nanoscratch tests

The nanoscratch tests were performed with the aforementioned Hysitron TriboLab instrument. The transducer has the ability to apply loads in the range of 1–10000 μN with a high load resolution of 1 nN, while the maximum penetration depth that can record is 3000 nm (3 μm) with a resolution of 0.04 nm. The instrument allows the measurement of both lateral load and normal displacement (scratch depth) while scratching. A three-sided pyramidal Berkovich diamond indenter (120 nm radius of curvature) was used for the scratch tests, which were performed at various normal forces ranging from 500 to 6000 μN , at a 20 μm scratch path, with a steady tip velocity of 1 $\mu\text{m/s}$. Coefficient of friction (μ) is calculated

as the ratio of lateral load to normal force. Nanoscratch experiments at the as deposited samples and after submersion in a cell culture medium were performed in a clean area environment with ~45% humidity and 23 °C ambient temperature [15]. Samples were submerged for 2 h at 12 mL of a cell culture medium (MEM alpha modification, pH 7.4, composition: amino acids, vitamins, sugars, inorganic salts, 1% fetal bovine serum) at 24 °C, following rinsing with H₂O. The segments of a scratch test are presented in Fig. 1. The post-scratch segment provides information on the remained plastic deformation, the elastic recovery and/or the delamination of the synthesized coatings. Tests at each applied load are repeated totally 5 times, in order to estimate the homogeneity of the synthesized samples and calculate the average μ values. The instrument, employed in this study, is also equipped with a Scanning Probe Microscope (SPM), in which the probe tip is moved in a raster scan pattern across sample surface using a three-axis piezo positioner. Through SPM images and data analysis, it is possible to investigate the adhesion properties and the wear resistance of the synthesized coatings.

3. Results and discussion

3.1. Nanoindentation results

In Table 1, the H and E_r values at the 10% of coatings thickness, before and after submersion in the cell culture medium, are tabulated. The values presented in Table 1 are the average of 6 tests, with corresponding error bars. No indentation, neither scratch tests were performed on the organic coating after submersion in the cell culture medium, because PDMAEMA is soluble in H₂O, resulting in the dissolution of the polymer coating [16]. From the data of Table 1, it is observed that the softest material, presenting the lowest H and E_r values, is the organic coating. Hybrid 1 coating reveals the highest H values because of the high MAPTMS – ZPO content, compared to hybrid 2 and organic coatings. However, hybrid 2 coating before submersion in the cell culture medium presents the highest E_r values, and its H values are in agreement with literature [17,18]. After submersion of the samples in the cell culture medium, it is observed that H and E_r values of hybrid 1 coating decrease, because of the remained –OH groups, due to the incomplete reaction of the inorganic network formation [19]. On the contrary, hybrid 2 coating presents an enhancement in the measured H and E_r values, probably attributed to H₂O absorption. Details of the nanomechanical properties of the synthesized coatings are presented in our previous work [9].

3.2. Nanoscratch results

Scratch tests were first performed on a glass substrate, in order to evaluate the μ values. It is observed that the glass substrate μ values decrease from a maximum value of ~0.5 to a value of ~0.25. Fig. 2a and b presents the μ evolution as a function of the scratch path at 500 and 2000 μN applied normal forces, respectively. It is observed that as the indenter first enters and moves toward the samples, μ values are higher than unity, indicating that higher forces hinder the initial movement of the indenter (static friction), whereas lower forces are observed when the motion has begun

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